

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
19 December 2002 (19.12.2002)

PCT

(10) International Publication Number  
**WO 02/101140 A1**

(51) International Patent Classification<sup>7</sup>: **D06M 15/61**,  
15/356, D06P 1/54 // 1:38

(21) International Application Number: PCT/US02/18276

(22) International Filing Date: 10 June 2002 (10.06.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
60/297,558 11 June 2001 (11.06.2001) US

(71) Applicant (*for all designated States except US*): **NANO-  
TEX, LLC** [US/US]; 5770 Shellmound Street, Emeryville,  
CA 94608 (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,  
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,  
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,  
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,  
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG,  
SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ,  
VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),  
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),  
European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR,  
GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent  
(BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR,  
NE, SN, TD, TG).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **MILLWARD, Dan,  
B.** [US/US]; Apt. D, 2111 Alameda Avenue, Alameda, CA  
94501 (US). **WARE, William, Jr.** [US/US]; 4145 Alpine  
Road, Portola Valley, CA 94028 (US).

(74) Agent: **LARSON, Jacqueline, S.**; Law Office of Jacque-  
line S. Larson, P.O. Box 2426, Santa Clara, CA 95055-2426  
(US).

**Published:**

- with international search report
- before the expiration of the time limit for amending the  
claims and to be republished in the event of receipt of  
amendments

*For two-letter codes and other abbreviations, refer to the "Guid-  
ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.*

(54) Title: MODIFICATION OF FABRIC FIBERS

(57) Abstract: This invention is directed towards fibers of fabric or other fibrous substrates coated with amine-containing polymers. These polymers impart durable anti-microbial activity, renewable control of certain odors, and the capacity to bind certain materials to the substrate surface.

WO 02/101140 A1

## **MODIFICATION OF FABRIC FIBERS**

### **Field of the invention:**

5        This invention is directed towards fibers of fabric or other fibrous substrates coated with amine-containing polymers. These polymers impart durable anti-microbial activity, renewable control of certain odors, and the capacity to bind certain materials to the fabric surface.

### **Background of the invention:**

      Fabrics composed of only natural (e.g. cotton, wool, silk) or synthetic (e.g. polyester, nylon, acrylic) fibers are often lacking in desirable attributes. It is common in the textile industry to add a small weight component of various chemicals to the fabric to impart desired properties; these treatments are commonly  
15        referred to as "finishes". Such chemical enhancers include dyes, optical brighteners, softeners, water repellents, water/oil repellents, insect repellents, anti-microbial and/or anti-fungal treatments, anti-static finishes, and hydrophilic finishes.

      Durability is simultaneously a desired property and a significant challenge for any finish. Even molecules with only slight volatility will eventually evaporate;  
20        sunlight and air will slowly degrade others. Cleaning procedures such as laundering, dry-cleaning, and shampooing are the most significant challenges to fabric finish durability. Many finishes are removed from fabrics after only a few cleanings.

      Various approaches have been taken to provide durable finishes. One  
25        method is to deposit chemicals, typically polymers, that are not readily solubilized and washed away after being precipitated onto the fabric. Alternatively, the active ingredient of a finish may be embedded in a laminant film that is applied to fabric; this procedure often allows for the slow release of the active ingredient into the surrounding fabric. However, the detergents and mechanical agitation of  
30        conventional cleaning procedures often eventually remove the polymer or laminant film when it is merely deposited onto the fiber surface.

      When the fabric fibers contain available reactive groups such as in cotton, linen, wool, or silk, the finish may be bound to the fabric through covalent chemical

bonds. This approach is very effective, but limited to a subset of fibers and finishes. One disadvantage to man-made fibers (e.g., regenerated cellulose, rayon or certain non-synthetic polyesters) and synthetic fibers (e.g. acrylic, lycra, polyester and nylon) is the essential absence of available reactive groups; the vast majority of such groups are used up in forming the polymer backbone. Thus it is difficult to attach a substantial amount of a finish to synthetic fibers via covalent bonding, and so this effective method of achieving finish durability is useless with synthetic fibers.

It would be desirable to provide a method for encasing fabric fibers, particularly synthetic fibers, in a polymeric coating. In this manner, the fibers would provide a structural support for the polymer sheath and enhance the polymer's durability to conventional cleaning processes such as laundering and dry cleaning. The polymer would provide desired characteristics to the fabric, potentially including the presentation of reactive groups on the fiber surface that could serve as attachment points for further fabric finishing. Hereinafter is described some "desired characteristics" that might be imparted by a finish.

US Patent 6,187,856, issued to Incorvia et al, teaches the use of crosslinked resins, formed from polyamidoamines and polychlorohydrin crosslinkers, to form durable films on fabrics. The resins of this patent are claimed to give durable anti-static properties to the fabric. Durability is defined in this patent as evidence of anti-static properties after dipping treated fabric into water heated at 80 °C for two twenty-minute intervals.

Anti-microbial finishes are highly desirable for many textile applications. They may be employed on fabrics used in settings requiring antiseptic conditions, such as in hospitals. They may also be useful for fabrics worn or used in commercial food preparation, hospitality settings, and other areas where there is the significant potential of exposing people to infectious bacteria.

There are only a handful of classes of anti-microbial compounds. Durability is a significant problem for them as most are small molecules that evaporate readily or can be washed away. Moreover, many anti-microbial compounds exhibit toxicity to humans. It would be desirable to invent a durable anti-microbial fabric finish that is innocuous to humans.

Various short (fifty amino acids or less), cytotoxic polypeptides have been identified (Maloy, et al., Biopolymers (Peptide Science) 37: 105-122 (1995)). They

share the common trait of a high content of arginine and lysine residues, and carry a net positive charge at physiological pH. The mechanism of toxicity appears to be cell lysis mediated by electrostatic coordination of the peptide to the cell wall.

US Patent 5,300,287, issued to Park, teaches the derivatization of  
5 polyethyleneimine, particularly with polyethylene glycols, to form graft polymers which exhibit antimicrobial and antifungal activity. These polymers are particularly directed towards use in ophthalmic products and contact lens care solutions.

US Patent 6,034,129, issued to Mandeville et al, teaches the use of cationic  
10 polymers to treat bacterial infections in mammals, specifically humans. The polymers described in the patent have amino or ammonium groups pendant from the polymer backbone.

The ability to eliminate or significantly diminish malodorous axillary (body) odor and foot odor is a desirable attribute for apparel fabrics. The chemical components of axillary odor are the waste by-products of certain bacteria that live  
15 off of the secretions from human sweat glands. These species of bacteria are called *lipophilic diphtheroids*. Some three dozen molecules with potentially offensive odors have been identified in body odor (see, Preti, G. et al, *J. Chem. Ecology*, 1991, **17**, 1469; Preti, G. et al, *J. Chem. Ecology*, 1992, **18**, 1039; Preti, G. et al, *J. Chem. Ecology*, 1996, **22**, 237; *Proc. Nat. Acad. Sci. USA*, 1996, **93**, 6626). All of them are  
20 organic acids and the main contributor to the odor has been identified as *trans*-3-methyl-2-hexenoic acid. The chemical components of foot odor have similar origin; they are waste products of the bacteria *brevidium epidermis*. These molecules are also organic acids, and the most significant component is isovaleric acid (see, Kanda, F. et al, *Brit. J. of Dermatology*, 1990, **122**, 771). It would be desirable to  
25 have a durable finish that would eliminate or significantly diminish malodorous body odor on fabrics. One approach is to include a bacteriocidal finish. However, these may not kill bacteria living on the skin and so odor may still be produced. Another method is to use a finish that absorbs the malodorous organic acids responsible for axillary and foot odor so that the volatile concentrations of the offensive organic  
30 acids are below the threshold of detectability. It would be greatly desirable to be able to recharge the absorptive capacity of such a finish by standard cleaning procedures.

US Patent 4,244,059, issued to Pflaumer, teaches the use of a water-soluble amine-containing polymer, Tydex-12 (Dow Chemical Co.), as an "odor absorbent compound". Tydex-12 is applied to a soft, air-permeable fabric composed of cellulosic fibers, and the treated fabric is then used in the manufacture of panty-type garments. The treated fabric is designed to absorb odors emanating from the vagina and surrounding region. The patent makes no claims as to durability, nor does it make provisions to provide for durability of the polymer to the fabric during common cleaning processes such as laundering.

WO patent 97/34040, issued to Koizumi et al., teaches the use of polyamines as coatings for acrylic fibers to produce deodorizing fibers. In this patent, wet gel acrylic fibers containing acid groups are brought into contact with "an amino compound" with the stoichiometry adjusted so that there is an excess of amine groups. Electrostatic interactions between the amines and acid groups presumably are the source of durability. The fibers have been wet spun and not previously dried. After contacting the amine compound, the coated fiber is heated at between "100 and 180 °C under wet heat conditions." Fiber products constructed from these fibers are able to deodorize acidic odors.

### SUMMARY OF THE INVENTION

This invention is directed towards durable finishes for fabrics and other fibrous substrates. The active components of the finishes are amine-containing polymers with reactive groups. The polymers become cross-linked on the substrate fiber surface and form a soft resinous coating that is durable to cleaning procedures. The reactive groups of the amine-containing polymer may be amines, but are not restricted to this functional group.

This invention is further directed to the fibers; yarns; woven, knitted or nonwoven fabrics and textiles; and finished goods (encompassed herein under the term "fibrous substrates") treated with the amine-containing polymeric coating of the invention.

The fibrous substrates treated with the finish described herein take on properties that are not found in the native fabric, including anti-microbial properties and/or the ability to eliminate or greatly diminish the most offensive component of malodorous body odor. When applied to synthetic fabrics, such as polyester or

nylon, the reactive groups of the present invention provide attachment points to make other finishes with reactivity complimentary to the amine-containing polymer (applied previously, simultaneously or in a later process) durable to cleaning procedures. This heightened durability can be brought about through the formation of ionic or covalent bonds with the reactive groups and/or to the amine groups of the present invention. The polymer coating also provides new opportunities for fabric dyeing. For example, reactive dyes can form covalent bonds with the amine-containing polymer and thus be used for dyeing synthetic fibers.

## DETAILED DESCRIPTION OF THE INVENTION

As used herein and in the appended claims, "a" and "an" mean one or more, unless otherwise indicated.

The term "durable" or "durability" as used herein describes a finished fibrous substrate in which the desired properties imparted to the substrate by the finish are observed after multiple launderings or dry cleanings.

For the purposes of this description and the accompanying claims, the term "amine-containing polymer" refers specifically to polymers that contain amine groups either within or pendant from the polymer backbone. For the purpose of this description, the term "amine group" describes primary, secondary and/or tertiary amine groups. The polymer may also contain quaternary amine groups, but the inclusion of quaternary amine groups without primary, secondary, or tertiary amine groups is insufficient to qualify such a polymer as an "amine-containing polymer" as described herein. The amine-containing polymer also contains reactive groups; these reactive groups may be but are not restricted to amine groups. Examples of alternative reactive groups include, but are not limited to, hydroxyls, thiols, and carboxylic acids.

The amine-containing polymer may be a homopolymer, copolymer, or terpolymer, and may come from natural sources or from synthetic preparation. Examples of amine-containing polymers from natural sources include amine-containing polysaccharides and amine-containing polypeptides. In a presently preferred embodiment, chitosan is such a natural polymer. Examples of synthetic amine-containing polymers include polyethyleneimine (PEI) and PEI derivatives, poly(vinylamine), poly(diallylamine), poly(allylamine), copolymers of diallylamine and

allylamine, co-and terpolymers containing diallylamine and/or allylamine, and condensation polymers formed from polyamine monomers and monomers with two or more amine-reactive groups. Other examples of amine-containing polymers are poly(acrylates) composed entirely or in part of acrylate monomers which contain  
5 amine groups, poly(methacrylates) composed entirely or in part of methacrylate monomers which contain amine groups, and co- or terpolymers composed of acrylate, methacrylate and/or other vinyl monomers, in which polymers at least some and potentially all of the monomers contain amine groups.

Presently preferred embodiments of the invention include the synthetic  
10 polymers PEI and PEI derivatives, poly(vinylamine), and polymers containing diallylamine or allylamine. PEI can be derivatized with molecules containing such reactive groups as halohydrins, epoxides, organic acids,  $\alpha,\beta$ -unsaturated organic acids, and carbonyls. PEI polymers and derivatized PEI polymers are commercially available from Nippon Shokubai and BASF. A presently preferred polymer is an  
15 epichlorohydrin-grafted PEI available from BASF under the trade name of Lupasol SC-86X.

The term "cross-linkers" as used herein describes molecules that contain two or more functional groups that form bonds with the reactive groups of the amine-containing polymer. The cross-linkers bind the amine-containing polymers together  
20 to form coatings of polymer film around the fibers. Fibers that contain reactive functional groups may also react with the cross-linkers to adhere the amine-containing polymer coating directly to the fiber.

In one embodiment, the amine groups of the amine-containing polymer are also the reactive groups used to form the durable fiber coating. Polymers that  
25 contain primary and/or secondary amines are particularly preferred in this embodiment. Those of skill in the art of chemistry will recognize that primary and secondary amines possess much greater versatility in bond formation than do tertiary amines, thereby broadening the types of potential cross-linkers. The reactive groups of the cross-linker should be present in sufficient quantity to form  
30 the durable coating, but preferably in a sub-stoichiometric amount relative to the amine groups of the polymer, particularly when a second finish will later be made durable by reaction with the amine-containing polymer. It is particularly desirable in this embodiment that the cross-linker reactivity be significantly amine-selective, so

that the cross-linkers react efficiently to bind the polymers together. In one embodiment, it is also desirable, but not required, that the basicity of the nitrogen atoms that participate in the cross-linking reaction be substantially unchanged after the reaction. Specific amine-reactive groups include alkyl halides, isothiocyanates, isocyanates, acyl azides, N-hydroxysuccinimide esters, sulfonyl chlorides, aldehydes, glyoxals, epoxides, oxiranes, carbonates, arylating agents, imidoesters, carbodiimides, anhydrides, and halohydrins. In a presently preferred embodiment, the cross-linker contains halohydrin or epoxide reactive groups. Examples of these cross-linkers are 1,3-dichloro-2-propanol and 1,4-butanediol diglycidyl ether (Sigma-Aldrich Corporation).

In another embodiment, the amine-containing polymer also contains non-amine reactive groups. The presence of non-amine reactive groups is particularly valuable when the amine groups of the polymer are exclusively or almost exclusively tertiary amine groups. Examples of non-amine reactive groups that are of use in the present invention include hydroxyls, thiols, and carboxylic acids. In a presently preferred embodiment, the reactive groups are hydroxyls. It is particularly desirable that the cross-linking reaction does not affect the basicity of the amines in the resulting film. A catalyst may optionally be included to facilitate cross-linking. Hydroxyl-reactive functional groups include epoxides, halohydrins, oxiranes, carbonyl diimidazole, N,N'-disuccinimidyl carbonate or N-hydroxysuccinimidyl chloroformate, alkyl halogens, isocyanates, and N-methylol ureas. Thiol groups react with haloacetyl and alkyl halide derivatives, maleimides, aziridines, acryloyl derivatives, arylating agents, and thiol-disulfide exchange reagents such as pyridyl disulfides, disulfide reductants, and 5-thio-2-nitrobenzoic acid. Carboxylate reactive groups include diazoalkanes and diazoacetyl compounds, oxazolines, carbonyl diimidazole, carbodiimides, and N-methylol ureas. Preferred cross-linkers are diepoxides (Sigma-Aldrich corp.), N-methylol ureas such as dimethyloldihydroxyethyleneurea (DMDHEU) (PatCoRez P-53, BFGoodrich), and blocked polyisocyanates such as Repearl MF (Mitsubishi Chemical Co.).

The finish that is applied to the fibrous substrate is a solution comprising at least an amine-containing polymer, a cross-linker, and a volatile solvent. It is desirable that the polymer and the cross-linker be soluble in the solvent. A particularly preferred solvent is water. The pad solution preferably contains amine-



containing polymer at between about 0.01% and about 75% by weight, more preferably about 0.05% and about 50% by weight, and most preferably about 0.1% and about 40% by weight. The pad solution preferably contains a cross-linker at between about 0.001% and about 40% by weight, more preferably about 0.01% and about 30 % by weight, and most preferably about 0.05% and about 20% by weight. The finish solution may also include other components as described below.

In a particular embodiment of the invention, the amine-containing polymer is partially reacted with a cross-linker *prior* to being placed in the treatment bath, e.g. substantially only one of the two or more reactive groups of the cross-linker pre-reacts with the amine-containing polymer. The resulting grafted polymer is then added to a treatment bath and applied to fabric, after which the fabric is cured to complete the reaction with the cross-linker. The grafted polymer may be the only component of the treatment bath; alternately other components such as additional cross-linkers and wetting agents may be included.

The reaction of the amine-containing polymer with certain cross-linker functional groups, such as halohydrins, results in the formation of mineral acids that lower the pH of the finish and may slow the rate and decrease the extent of cross-linking. To control this deleterious effect, a buffering agent may be added to the finish solution. Buffering agents are weak acids or bases that tend to hold solutions containing them within  $\pm 1$  pH point of the buffering agents'  $pK_a$ . One skilled in the art will appreciate that an optimal buffer solution consists of equimolar portions of the buffering agent and its corresponding conjugate acid or base, the latter often being formed by addition of a strong acid or base. Lists of buffering agents can be found in *Lange's Handbook of Chemistry*, 14<sup>th</sup> edition, ed. J.A. Dean, McGraw-Hill, Inc., section 8, p.p. 103-112. If used, a buffering agent should be chosen so that the  $pK_a$  of the buffer lies within the optimal pH range of the reaction. This pH range is dependent on the identities of the reactive group of the amine-containing polymer and of the cross-linker. The buffer must also be chosen so as to be unreactive with the cross-linker or the amine-containing polymer. The amount of buffering agent should be slightly more than equimolar to the theoretical total amount of acid generated by complete reaction of the cross-linker.

The finish solution may also include other additives. For example, amine groups are prone to oxidation, the by-products of which are often yellow-brown in

color. The addition of an anti-oxidant to the finish solution can minimize the extent of oxidation both in the stored state and while the finish is being applied and cured on the fabric. A presently preferred anti-oxidant is phosphoric acid. Optical brighteners (such as, for example, the Leucophor products from Clariant Corp. or the Uvitex products from Ciba Corp.) may be included in the finish solution.  
5     Whitening agents, such as sodium tetraborate, may also be included in the solution. The finish solution may also contain a wetting agent, such as WetAid NRW (BFGoodrich Corp.), to aid the equal spread of the finish over the fibers. This is particularly useful when the fiber material is hydrophobic. Additional additives can  
10    be added to the solution as needed.

      The finish can be applied to the fibrous substrate by exposing the substrate to the finish solution by methods known in the art, such as soaking, spraying, dipping, fluid-flow, and padding. The exposed fibrous substrate is then heated to remove the volatile solvent and to speed up the reaction of the polymer with the  
15    cross-linker. Alternatively, the fibers or yarns may be exposed to the finish solution by soaking, spraying or dipping. After the finish is cured in place, the fibers or yarns may be woven or knit into fabrics.

      The finish solution may be applied to the fibrous substrate at any temperature above the freezing point and below the boiling point of the solvent. In the present  
20    embodiment, the application temperature is preferably between 5 and 90 °C, more preferably between 10 and 50 °C, and most preferably at room temperature. The treated fabric should be cured at a temperature high enough to induce formation of the sheath in a very short time, preferably less than five minutes, more preferably a minute or less. In the present embodiment, the curing temperature is preferably  
25    between 100 and 180 °C, more preferably between 110 and 140 °C.

      The present invention is further directed to the fibrous substrates treated with the finish described above. Substrates thus treated will possess properties not found in untreated substrates. These properties may include anti-microbial properties and the ability to absorb malodorous organic acids via acid-base  
30    reactivity of the acids with the amine groups of the finish. In the case of substrates constructed all or in part of inert, synthetic fibers, the treated fibers present reactive groups on their surfaces. A further treatment with a second finish containing groups that react with the modified fibers will result in durability for the second finish.

Examples of desired durable second finishes include dyes, softeners, water repellents, water/oil repellents, insect repellents, anti-microbial and/or anti-fungal treatments, anti-static finishes, and hydrophilic finishes.

5 In one embodiment of the invention, the treated fibrous substrate has antimicrobial properties. Fabrics and other fibrous substrates that either prevent the growth of or actively kill bacteria, mold, or fungi are very desirable, particularly in settings where biologically contaminated fabrics can be the source of infection such as in hospital and food preparation settings. The finish of the present invention has been shown to provide durable, non-leaching antimicrobial properties to treated  
10 fabrics. Not to be bound by theory, it is believed that the action of the finish can be attributed to the cationic charge of the polymer. The cell walls of microbes are composed primarily of negatively charged phosphate lipid bilayers. In theory, the electrostatic coordination of the lipid bilayer to the finish polymer disrupts the cell wall and kills the organism.

15 Another embodiment of the present invention is the preparation of treated fibrous substrates that absorb and deodorize organic acids, which gives such substrates the ability to eliminate or greatly diminish offensive body odor. The odor-absorbing capacity of the fabric can be recharged when necessary by conventional laundering procedures. The molecular sources of offensive body odor are primarily  
20 the waste products of a species of bacteria named *lipophilic diphtheroids*. This species of bacteria lives on the skin surface of humans and primarily digests the secretions of the apocrine glands. The malodorous waste products of *lipophilic diphtheroids* are organic acids, with the most significant component being 3-methyl-2-hexenoic acid. Volatile organic acids are commonly considered to have highly  
25 offensive odors even in extremely low concentrations. The odor-absorptive capacity of the treated fibrous substrate stems from the basicity of the amine groups of the finish. Acids react with the free amine groups of the amine-containing polymer to form non-volatile ionic complexes. The extent to which this ionic complexation occurs depends on the relative strength of the acid and base. In the case of the  
30 present invention, the reaction is biased towards formation of the ionic complex to such a degree that only between one acid molecule in ten thousand to one acid molecule in a million would be found in the non-ionized, potentially volatile form. Thus, as long as unreacted amine groups are available in the treated fabric, the

concentration of volatilized organic acid around the treated fabric will be lowered to the point of being undetectable or scarcely detectable.

An advantage to the present invention over conventional odor-absorbing material such as activated carbon is the ability to recharge the odor-absorptive capacity of the fibrous substrate. As amines are weak bases, exposing the substrate to an aqueous solution with a pH at or above the  $pK_b$  of the base will deprotonate most of the amine complexes and result in separation of the amine-acid complexes. The conjugate base forms of the malodorous organic acids will be washed away in the laundry liquor, leaving behind free amine groups on the fiber surface. A pH of 10 is above the  $pK_b$  of most amines, and laundry detergent solutions such as Tide<sup>®</sup> typically have this pH or higher. Therefore, a conventional laundering procedure is sufficient to recharge the odor-absorptive capacity of the fabric.

A further embodiment of the present invention is the preparation of a fiber surface with reactive amine groups that can participate in binding other finishes to the fibrous substrate in a durable fashion. This is particularly useful when the fiber is composed of polymers without a significant number of reactive groups, such as in polyester and nylon. The fibers treated with the amine-containing polymeric finish of the present invention present reactive groups on their surfaces. A further treatment with a second finish containing groups that react with the modified fibers will result in durability for the second finish. Examples of desired durable second finishes include dyes, softeners, water repellents, water/oil repellents, insect repellents, anti-microbial and/or anti-fungal treatments, anti-static finishes, and hydrophilic finishes.

The nature of the reactive functional group of a second finish is dependent on the reactive groups of the amine-containing polymer, as described *vide supra*. Examples of amine-reactive groups include isothiocyanates, isocyanates, acyl azides, N-hydroxysuccinimide esters, sulfonyl chlorides, aldehydes, glyoxals, epoxides, oxiranes, carbonates, arylating agents, imidoesters, carbodiimides, anhydrides, and halohydrins. Hydroxyl-reactive functional groups include epoxides, halohydrins, oxiranes, carbonyl diimidazole, N,N'-disuccinimidyl carbonate or N-hydroxysuccinimidyl chloroformate, alkyl halogens, isocyanates, and N-methylol ureas. Thiol groups react with haloacetyl and alkyl halide derivatives, maleimides, aziridines, acryloyl derivatives, arylating agents, and thiol-disulfide exchange

reagents such as pyridyl disulfides, disulfide reductants, and 5-thio-2-nitrobenzoic acid. Carboxylate-reactive groups include diazoalkanes and diazoacetyl compounds, carbonyl diimidazole, carbodiimides, and N-methylol ureas.

The following examples are intended for illustrative purposes only. Those of skill in the art will recognize other embodiments, all of which are considered part of the present invention.

## EXAMPLES

### 10 Example 1.

A 100.0 g solution of 10% polyethyleneimine (PEI, Mol. Wt. 70,000, Nippon Shokubai) and 5% 1,3-dichloro-2-propanol (DCP, Aldrich Chemical Corp.) at pH 9.0 was prepared by combining 33.3 g of PEI (30% solution) and 50.0 g water, adjusting the pH with hydrochloric acid (VWR), adding additional water to make up mass to 15 95.0 g, and then adding 5.0 g DCP. A swatch of undyed, woven, microdenier polyester fabric was dipped in this solution, processed through pad rollers or "padded", and cured in a forced-air oven at 121 °C for five minutes. A control swatch (C-1) of the same fabric was dipped in water at pH 9.0, and a second control swatch (C-2) was dipped in 10% PEI at pH 9.0. All control swatches were padded and then cured in a forced-air oven at 121 °C for five minutes. All of the swatches 20 were cut into quarters. One set of quarters was rinsed individually under cold tap water for 20 minutes; this set is referred to herein as the zero (0) home laundering (HL) samples. The remaining three sets of quarters were machine laundered five, ten or twenty times according to the American Association of Textile Chemists and Colorists (AATCC) method 124-1996, reported in the AATCC technical manual 25 (1999). Upon completion of laundering, all of the quarters were cut in half. One set of halves was dyed as described below, the other set of halves was used for analysis of odor absorption.

The sample swatches to be dyed were placed in a 0.1% aqueous solution of dye Acid Red 37 (20:1 liquor:goods ratio) for thirty (30) minutes. Upon completion 30 of dyeing, the samples were removed from the dye bath and rinsed individually under cold tap water for one minute. The degree of coloring was noted and recorded in Table 1 under the column headings of "Color" ("d." = dark, "l." = light).

Untreated polyester has little or no affinity for acid dyes, whereas PEI has a strong affinity for acid dyes, so this test is an excellent indication of the presence of PEI.

The odor analysis was performed as follows: one drop of a 0.01% butyric acid solution was placed onto each swatch, then the drop was allowed to dry. A panel of judges then smelled each swatch and rated the odor as strong, faint, or not noticeable. The generalized impressions of the judges are recorded in Table 1 under the column headings of "Odor".

Table 1

Sample	0 HL		5 HL		10 HL		20 HL	
	Color	Odor	Color	Odor	Color	Odor	Color	Odor
Treated	d. red	none	red	none	red	none	l. red	faint
C-1	red	strong	white	strong	white	strong	white	strong
C-2	d. red	none	l. pink	strong	white	strong	white	strong

### Example 2.

A solution of 4% PEI (BASF, Mn=60,000), 3% 1,4-butanedioldiglycidyl ether (Sigma-Aldrich Corp.), and 0.1% WetAid NRW (BFGoodrich) was prepared by combining 24.0 g PEI, 0.3 g WetAid NRW and 2400.0 g distilled water in a beaker. The pH of this solution was adjusted to 9.0 with 85% phosphoric acid (Baker). Sufficient water to bring the combined mass up to 291.0 g was added, followed by 9.0 g of 1,4-butanedioldiglycidyl ether. The formulation (Formulation A) was then stirred thoroughly.

Formulation B was an aqueous solution of 4% PEI and 0.1% WetAid at pH 9.0 (300.0 g).

Formulation C was an aqueous solution of 3% 1,4-butanedioldiglycidyl ether and 0.1% WetAid (300.0 g).

Formulation D was an aqueous solution of 0.1% WetAid (300.0 g) adjusted to pH 9.0 with sodium hydroxide (Aldrich.).

Swatches of three styles of polyester fabric and a cotton fabric were dipped in each solution. The swatches were then padded to a uniform wet pick-up, and then dried at 157 °C for fifteen seconds past the point of fabric dryness. The samples

were then laundered thirty times according to the AATCC method 124-1996. Small swatches were cut from the fabric before laundering and after one and thirty launderings. Odor absorption testing was performed on each small swatch as described in Example 1.

5           The swatches treated with Formulation A absorbed odors after 30 launderings, whereas the other treated samples did not.

### Example 3.

10           Formulation A, a 500.0 g solution of 5% ethoxylated PEI (BASF), 0.1% WetAid NRW (BFGoodrich) and 3% 1,4-butanedioldiglycidyl ether (Sigma-Aldrich Corp.), was prepared by combining 67.5 g ethoxylated PEI, 0.5 g WetAid and 417.0 g water. 15.0 g 1,4-butanedioldiglycidyl ether was then added and the solution was stirred thoroughly.

          Formulation B consisted of a 500.0 g 0.1% WetAid solution.

15           Swatches of three woven polyester styles, a cotton knit, and a 90/10 cotton/lycra knit were cut and dipped in one of the two formulations. The swatches were padded to a uniform wet pick-up, then dried at 157 °C for fifteen seconds past the point of fabric dryness. The samples were then laundered thirty times according to the AATCC method 124-1996. Small swatches were cut from the fabric before  
20   laundering and after one and thirty launderings.

          Odor absorption testing was performed on the swatches laundered thirty times using 0.01% butyric acid. A panel of judges compared the odor of the treated samples to the untreated controls. The controls were assigned a value of three (3). If no odor could be detected on the treated swatch, it was assigned a value of zero  
25   (0). Any detectable butyric acid odor on the treated fabrics were ranked from one to three relative to the control. The thirty-home laundering small swatches were also dyed according to the procedure described in Example 1.

          The results from the dyeing and smell testing are tabulated in Table 2. The polyester swatches are identified as PET#, the cotton as COT, and the cotton/lycra  
30   blend as C/L. A suffix of T indicates treatment with formulation A, the suffix U indicates treatment with formulation B.

Table 2

Sample ID	panelist 1	panelist 2	panelist 3	Average	StdDev	dyeshade
PET1-T	0	0	0	0.00	0.00	pink
PET1-U	3	3	3	3.00	0.00	white
PET2-T	1	0	0	0.33	0.58	pink
PET2-U	3	3	3	3.00	0.00	white
PET3-T	0	0	0	0.00	0.00	pink
PET3-U	3	3	3	3.00	0.00	white
COT-T	0	0	0	0.00	0.00	red
COT-U	3	3	3	3.00	0.00	pink
C/L-T	0	0	1	0.33	0.58	red
C/L-U	0	3	3	2.00	1.73	pink

5

Example 4.

A 100.0 g portion of 30% PEI (Nippon Shokunai, Mn=70,000) was combined with 7.8 g glycidol (Sigma-Aldrich). The glycidol was allowed to react with the PEI for 1.5 hours at room temperature. Complete reactivity between the polyethyleneimine and glycidol was assumed. The resulting product, a glycidol-grafted polyethyleneimine, is referred to hereinafter as PEI-g20. The PEI-g20 was used without further purification as a 35% aqueous solution.

A series of pad-bath formulations were prepared; all were adjusted to pH 3.5 with hydrochloric acid (VWR). Formulation A consisted of water. Formulation B consisted of 10% PatCoRez P-53 (DMDHEU resin, BFGoodrich). Formulation C consisted of 12.6% PEI-g20. Formulation D consisted of 10% PatCoRez P-53 and 12.6% PEI-g20. For each formulation, two swatches of cotton were dipped and then padded and dried/cured for three minutes. One swatch for each formulation was laundered five times according to the AATCC method 124-1996.

The swatches were then tested for anti-microbial activity according to AATCC test method 100. The results are recorded in Table 3. The sample IDs correspond to the formulation that the sample was dipped in. the term "TMTC" indicates the presence of too many bacterial colonies to count. It is noteworthy that the PEI-g20 provides an essentially instantaneous kill of the test bacteria both at zero and five home launderings (Samples C and D). The DMDHEU resin in PatCoRez P-53 also has anti-microbial activity, probably due to the slow release of formaldehyde as it decomposes (Sample B); however, the effect is much slower. The untreated control (Sample A) has no anti-microbial activity.



Table 3

Sample ID	# HLs	# of Colonies		
		0 hours	24 hours	% Kill
A	0	TMTC	TMTC	0%
	5	1589	TMTC	0%
B	0	TMTC	0	100%
	5	TMTC	0	100%
C	0	0	0	100%
	5	423	0	100%
D	0	428	0	100%
	5	0	0	100%

5

Example 5.

A 400 liter solution of 25% Lupasol SC-86X (BASF), 1.5% Repearl MF (Mitsubishi Chemical Co.) and 0.1% WetAid NRW (Noveon) was prepared and placed in a pad bath on a Montfort tenter frame. Six styles (1-6) of dry, open-width  
 10 100% polyester fabric moving at 23.5 yards per minute was passed through this solution, then through a squeeze roll pad set at 55 psi to achieve an average wet pick-up of 106%. The fabrics then passed through an oven set at 320 °F; the fabrics had a dwell time of 14 seconds at this temperature. The finished fabric was tested  
 15 laundered twenty times according to AATCC method 124-96 and tested again. Untreated swatches of the same six styles were also tested in the same fashion as a comparison. The results are recorded in Table 4.

The testing was performed as follows: A drop of a dilute butyric acid was placed on a swatch and allowed time to absorb into the fabric, then a panel of  
 20 judges would smell the swatch. If no odor could be detected by any of the judges, a drop of a more concentrated butyric acid solution was placed on the fabric and it was evaluated again. This procedure was repeated until all of the judges could smell the butyric acid. Each judge recorded the concentration of butyric acid (in parts per million) at which he was able to detect an odor; this concentration is  
 25 referred to as the odor score. The odor scores for each swatch were then averaged.

Table 4

Parameters		Average Odor Score	
Style	Treated (Y/N)	0 HL	20 HL
1	Y	1000	600
1	N	133	167
2	Y	667	667
2	N	83	117
3	Y	867	667
3	N	117	117
4	Y	1000	733
4	N	67	167
5	Y	1000	533
5	N	200	267
6	Y	1000	1000
6	N	67	467

## WHAT IS CLAIMED IS:

1. A finish for a fibrous substrate comprising an amine-containing polymer with reactive groups, a cross-linker, and a volatile solvent, and wherein the finish is durable to cleaning procedures.
2. A finish according to claim 1 which provides anti-microbial properties to the fibrous substrate.
3. A finish according to claim 1 which provides the fibrous substrate with the ability to eliminate or greatly diminish offensive body odor.
4. A finish according to claim 3 wherein the ability is rechargeable.
5. A fibrous substrate comprising amine-containing polymers crosslinked on the fiber surface of the fibrous substrate to form a resinous coating durable to cleaning procedures.
6. A fibrous substrate according to claim 5 which exhibits durable anti-microbial properties.
7. A fibrous substrate according to claim 5 which exhibits the durable ability to eliminate or greatly diminish offensive body odor.
8. A fibrous substrate according to claim 7 wherein the ability is rechargeable.
9. A fibrous substrate according to any one of claims 5 to 8 which is a synthetic fabric that further comprises at least one additional finish, wherein the additional finish is durable to cleaning procedures.
10. A fibrous substrate according to claim 9 wherein the additional finish is a reactive dye.

11. A method for providing anti-microbial properties to a fibrous substrate, the method comprising:

exposing the fibrous substrate to a treatment composition comprising an amine-containing polymer with reactive groups, a cross-linker, and a volatile solvent; and

curing the fibrous substrate;

to give a fibrous substrate exhibiting durable anti-microbial properties.

12. A method for providing a fibrous substrate with the ability to eliminate or greatly diminish offensive body odor, the method comprising:

exposing the fibrous substrate to a treatment composition comprising an amine-containing polymer with reactive groups, a cross-linker, and a volatile solvent; and

curing the fibrous substrate;

to give a treated fibrous substrate which exhibits the ability to durably eliminate or greatly diminish offensive body odor.

13. A method according to claim 12 which comprises the further step of exposing the treated fibrous substrate to an aqueous solution with a pH at or above 10, to recharge the odor-absorptive ability of the fibrous substrate.

14. A method for treating a synthetic fibrous substrate to provide durable finishes on the synthetic fibrous substrate, the method comprising:

exposing the fibrous substrate to a first finish comprising an amine-containing polymer with reactive groups, a cross-linker, and a volatile solvent to give a treated fibrous substrate with reactive groups on its surface;

curing the treated fibrous substrate; and

exposing the treated fibrous substrate to a second finish containing groups that react with the reactive groups on the treated fibrous substrate;

to give a synthetic fibrous substrate wherein the second finish is durable to cleaning procedures.

15. A method according to claim 14 wherein the synthetic fibrous substrate is exposed to the first and the second finishes simultaneously.

16. A method according to claim 14 wherein the synthetic fibrous substrate is  
5 exposed to the second finish after it is exposed to the first finish and either before or after the curing step.

17. A method according to any of claims 14 to 16 wherein the second finish is a reactive dye.

10

18. A method according to any of claims 11 to 17 wherein the amine-containing polymer is partially reacted with the cross-linker prior to being placed in the volatile solvent.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 02/18276

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 D06M15/61 D06M15/356 D06P1/54 //D06P1:38

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 D06M D06P

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 512 064 A (VON DER ELTZ ANDREAS ET AL) 30 April 1996 (1996-04-30)	1-12, 14, 16, 17
Y	examples	18
X	US 4 588 413 A (KEIL KARL-HEINZ ET AL) 13 May 1986 (1986-05-13)	1-8
Y	column 3, line 63 - column 4, line 3 examples	18
X	US 3 885 069 A (ROBERTS EARL J ET AL) 20 May 1975 (1975-05-20)	1-8
Y	column 1, line 28 - line 29 examples 1-6	12
	--- -/--	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

\* Special categories of cited documents:

\*A\* document defining the general state of the art which is not considered to be of particular relevance

\*E\* earlier document but published on or after the international filing date

\*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

\*O\* document referring to an oral disclosure, use, exhibition or other means

\*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*&amp;\* document member of the same patent family

Date of the actual completion of the international search

14 October 2002

Date of mailing of the international search report

11/11/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5618 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Flococo, M

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 02/18276

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	ZENG X. N. ET AL: "Analysis of characteristic odors from human male axillae" JOURNAL OF CHEMICAL ECOLOGY, vol. 17, no. 7, 1991, pages 1469-1491, XP008008746 cited in the application page 1488, line 13 - line 15 ----	12
X	US 4 806 126 A (STERNBERGER KLAUS ET AL) 21 February 1989 (1989-02-21) column 2, line 38 - line 45 examples ----	1-8
X	US 3 383 162 A (PITTMAN ALLEN G ET AL) 14 May 1968 (1968-05-14) column 30, line 43 -column 32, line 10 ----	1-8
A	US 4 778 813 A (FENYES JOSEPH G ET AL) 18 October 1988 (1988-10-18) column 3, line 39 - line 43 ----	11
A	GB 1 549 012 A (PROCTER & GAMBLE) 1 August 1979 (1979-08-01) page 1, line 54 - line 69 page 2, line 11 - line 20 -----	12

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 02/18276

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:  
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

### Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.



## FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

## Continuation of Box I.2

The initial phase of the search revealed a very large number of documents relevant to the issue of novelty. So many documents were retrieved that it is impossible to determine which parts of the claims may be said to define subject-matter for which protection might legitimately be sought (Article 6 PCT). For these reasons, a meaningful search over the whole breadth of the claims is impossible. Consequently, the claims have been searched with the restriction that the amine-containing polymer be one mentioned in the examples, i.e. poly(ethylene imine) or a poly(ethylene imine) derivative.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 02/18276

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5512064	A	30-04-1996	DE 4325783 A1	02-02-1995
			DE 59407370 D1	14-01-1999
			EP 0636742 A2	01-02-1995
			JP 7150477 A	13-06-1995
US 4588413	A	13-05-1986	DE 3329029 A1	28-02-1985
			AT 33409 T	15-04-1988
			DE 3470332 D1	11-05-1988
			EP 0133933 A2	13-03-1985
			JP 60052687 A	25-03-1985
			ZA 8406213 A	27-03-1985
US 3885069	A	20-05-1975	US 3976604 A	24-08-1976
US 4806126	A	21-02-1989	DE 3709766 A1	06-10-1988
			AT 72846 T	15-03-1992
			BR 8801364 A	01-11-1988
			CA 1319471 A1	29-06-1993
			DE 3868521 D1	02-04-1992
			EG 18505 A	30-04-1993
			EP 0284010 A2	28-09-1988
			GR 3004586 T3	28-04-1993
			JP 63256778 A	24-10-1988
			KR 9602654 B1	24-02-1996
			PH 25033 A	28-01-1991
			PT 87052 A ,B	01-04-1988
			TR 24316 A	12-09-1991
			ZA 8802102 A	28-06-1989
US 3383162	A	14-05-1968	US 3372978 A	12-03-1968
			US 3385653 A	28-05-1968
			US 3406005 A	15-10-1968
			BE 664664 A	16-09-1965
			FR 1455905 A	05-01-1967
			GB 1113604 A	15-05-1968
			NL 6506829 A	29-11-1965
			US 3433575 A	18-03-1969
			US 3440002 A	22-04-1969
			US 3632391 A	04-01-1972
US 4778813	A	18-10-1988	NONE	
GB 1549012	A	01-08-1979	AT 365424 B	11-01-1982
			AT 391976 A	15-06-1981
			AU 508522 B2	27-03-1980
			AU 1394576 A	17-11-1977
			BE 842314 A1	29-11-1976
			BR 7603411 A	21-12-1976
			CA 1102952 A1	16-06-1981
			CH 621469 A5	13-02-1981
			DE 2623652 A1	09-12-1976
			DK 237476 A	01-12-1976
			ES 221256 Y	16-04-1977
			FR 2312210 A1	24-12-1976
			IE 42696 B1	24-09-1980
			IT 1073961 B	17-04-1985
			JP 52021951 A	18-02-1977
			LU 75051 A1	15-02-1977

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 02/18276

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 1549012	A	NL 7605731 A	02-12-1976
		PH 11540 A	10-03-1978
		SE 7606101 A	01-12-1976
<hr/>			